Renewable and Sustainable Energy Reviews 16 (2012) 1899–1906

Contents lists available at SciVerse ScienceDirect

Renewable and Sustainable Energy Reviews

journal homepage: www.elsevier.com/locate/rser

A review of working fluids of absorption cycles

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ARTICLE INFO

Article history:
Received 21 February 2011
Accepted 5 January 2012
Available online 21 February 2012

Keywords:
Absorption heat pump
Working fluid
Absorption chiller
Absorption transformer

ABSTRACT

A complete review of working fluids of absorption cycles is presented. Absorption cycles contain absorption heat pumps, absorption chillers and absorption transformers. Working fluids are divided into five series according to different absorbents.

Contents

1. Introduction

Heating and cooling devices are widely adopted in industrial and resident applications. Besides, there is huge low grade heat in many industries, which could be reused to increase the energy efficiency. Among heat driven devices, absorption cycles (absorption heat pump, absorption chiller and absorption transformer) can use low grade heat in various industrial processes. Besides, absorption cycles can benefit the atmosphere by reducing the emission of carbon dioxide and adopting environment friendly working pair.

Absorption cycle has been developed in 1700s. And it is well known that ice could be made by the evaporation of pure H_2O from a vessel contained within an evacuated container in the presence of sulfuric acid [1]. Ferdinand Carre presented a novel machine using H_2O+H_2O as working fluids in 1859, which took out a US patent in 1860. This is the original design of absorption cycles.

An absorption cycle using $H_2O+LiBr$ was created in 1950s. The working fluid of an absorption cycle is combined by the refrigerant and absorbent. The basic principle of an absorption cycle is shown in Fig. 1.

The strong solution into the absorber will absorb refrigerant vapor due to its pressure difference with evaporator. The strong solution comes into weak solution after absorbing refrigerant, which is pumped into the generator to ensure this cycle continuously. Refrigerant vapor is gained by heating the weak solution, then, it is condensed in the condenser to ensure a constant pressure in both generator and condenser.

Performance of an absorption cycle is critically dependent on the thermodynamic properties of working fluids [2]. The mixture of absorbent–refrigerant should be chemically stable, non-toxic, and

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doi:10.1016/j.rser.2012.01.011

Nomenclature

2EH 2-ethyl-1-hexanol
AHP absorption heat pump
AHT absorption heat transformer
AC absorption chiller (absorption refrigeration)
DMAC N,N′-dimethylacetamide
DMETEG dimethyl ether tetraethylene-glycol
DMEU dimethyl-ethyleneurea
E181 tetraethylene glycol dimethyl ether
EMISE 1-ethyl-3-methylimidazolium ethylsulfate
MCL N-methyl ε-caprolactum
[MMIM][DMP] 1,3-dimethylimidazolium dimethylphosphate
NMP N-methy1-2-pyrrolidone
PYR 2-pyrrolidone
TFE 2,2,2-trifluoroethanol
TEGDME tetraethylene glyeol dimethyl ether

non-explosive. The requirements of working fluids of absorption cycles are listed [3]:

(1) The elevation of boiling (the difference in boiling point between the pure refrigerant and the mixture at the same pressure) should be as large as possible;
(2) Refrigerant should have high heat of vaporization and high concentration within the absorbent in order to maintain low circulation rate between the generator and the absorber per unit of cooling capacity;
(3) Transport properties that influence heat and mass transfer, e.g., viscosity, thermal conductivity, and diffusion coefficient should be favorable;
(4) Both refrigerant and absorbent should be non-corrosive, environmental friendly, and low-cost.

A critical review of absorption technologies was given, in which contained a short introduction of working fluids reported before 2001 [4]. Although lots of working fluids are given in the literature, there is not a complete review with comparison. In order to present different working fluids clearly, working fluids given could be divided into five series generally according to the choice of refrigerant in this work: NH_3 series, H_2O series, alcohol series, halogenated hydrocarbon series and other refrigerants.

2. Working fluids of absorption cycles

2.1. Series of refrigerant using NH_3

Since the invention of an absorption refrigeration system, $H_2O + NH_3$ has been widely used. Both NH_3 and H_2O are highly stable for a wide range of operating temperature and pressure. NH_3 is a good refrigerant due to its high latent of vaporization with a freezing point of −77 °C. Thermal properties of $NH_3 + H_2O$ could be found [5–10].

The performance of an absorption heat pump operating with $H_2O + NH_3$ and $NH_3 + H_2O + LiBr$ mixtures is compared. The COP of the absorption heat pump operating with a ternary mixture having a $H_2O + LiBr$ (mass ratio = 48:52) was, on average, 0.05 lower than with the binary system. However, several factors indicated that the refrigerant vapor entering the rectifier had significantly lower H_2O content with the ternary system [11]. Thermal properties of $H_2O + LiBr + NH_3$ were measured and correlated [12–14].

$H_2O + NH_3$ was compared with $NH_3 + LiNO_3$ in the two-stage vapor absorption refrigeration cycle, and they found that the COP was higher for $NH_3 + LiNO_3$ than that for $NH_3 + H_2O$ [15].

As we known, it is necessary to add a rectification device in absorption cycles using $H_2O + NH_3$, which was led by the incomplete separation of H_2O and NH_3 in the generator. NaOH was added to the $H_2O + NH_3$ to improve the separation of NH_3 in the generator and reduce both chiller driving temperature and rectification losses, and cycle simulation based on their experimental data showed that the COP was about 20% higher than the conventional

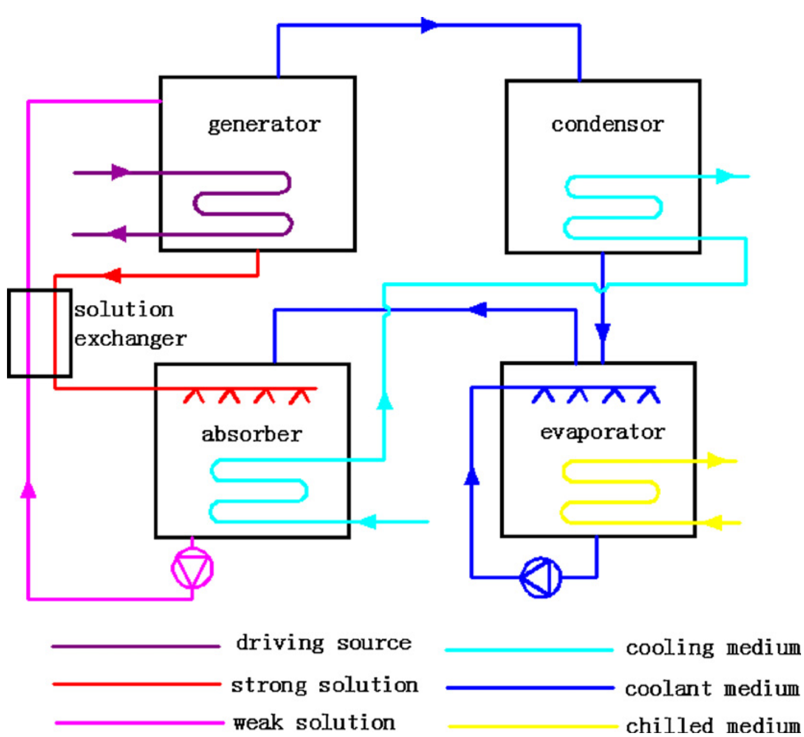


Fig. 1. The basic absorption cycle.

$NH_3 + H_2O$ under same conditions and using a hydroxyl separation efficiency of 99% for NaOH [16].

2.2. Series of refrigerant using H_2O

The LiBr + H_2O was used in absorption cycles around 1930 [17]. High latent of evaporation of H_2O and high temperature difference of boiling point between H_2O and LiBr ensured the rapidly development of this combination. Thermodynamic properties of LiBr + H_2O were studied [18–24].

Compared with refrigerant using NH_3, absorption cycles adopting H_2O + LiBr show higher efficiency, lower pressure and no-rectifying section [17]. H_2O + LiI showed similar performance with H_2O + LiBr when adopted in absorption cycles for heating [23,24].

Thermodynamic analysis was carried out to study the performance of single-stage, two-stage and double-absorption heat transformers operating with the water + Carrol mixture, where Carrol is a mixture of lithium bromide and ethylene glycol [$(CH_2OH)_2$] in the ratio of 1:4.5 by weight [25].

Besides, this working fluids were compared with LiBr + $H_2N(CH_2)_2OH$ + H_2O and LiBr + $(HOCH_2CH_2)_2NH$ + H_2O (LiBr + $H_2N(CH_2)_2OH$ and LiBr + $(HOCH_2CH_2)_2NH$ mass ratio = 3.5:1) in the air-cooled absorption cycle, and results indicated that all the solutions were found to be operated safely at high absorber and condenser temperatures with proper cooling capacity and COP [26].

A computer program able to handle different equipment arrangements was developed and the modeling of the $H_2O + CaCl_2$ and H_2O + LiCl systems in a single stage absorption heat transformer was developed, and better performance of the H_2O + LiCl system in this system can be expected compared to that for the $H_2O + CaCl_2$ pair from modeling results [29].

Measurements of thermo physical properties of the H_2O + LiBr + CH_3COOK system (salt mass ratio = 2:1) and the H_2O + LiBr + $CH_3CH(OH)COONa$ system (salt mass ratio = 2:1) were measured and proposed to be possible new working fluids for absorption heat pump [30].

$H_2O + CHO_2Na$ + LiBr (salt mass ratio = 2:1) was recommend as an alternative to H_2O + LiBr by comparing the mass transfer characteristics of H_2O vapor absorption into LiBr and organic salts of sodium and potassium (formate, acetate and lactate) [31]. Thermodynamic properties of H_2O + LiBr + CHO_2K (salt mass ratio = 2:1) and H_2O + LiBr + CH(OH)COONa (salt mass ratio = 2:1) were measured and recommended for the air-cooled absorption chiller [30]. On the purpose of reduction of vapor pressure of the H_2O + LiBr, H_2O + LiBr + CHO_2Na (salt mass ratio = 2:1) and H_2O + LiBr + CHO_2K (salt mass ratio = 2:1) were proposed [32]. CHO_2K was studied theoretically and experimentally in order to find an improved absorbent in absorption cycles due to its good thermodynamic properties, low toxicity and non-flammability [33]. Physical and thermal properties of the (H_2O + LiBr + CHO_2K) system and (H_2O + LiBr + CHO_2K) system were experimentally studied, which owed the advantage of low toxicity and non-flammability [32,33]. H_2O + LiBr + CHO_2K (salt mass ratio = 2:1) was compared with H_2O + LiBr in the absorption refrigeration cycle by a simulation program, which showed that H_2O + LiBr + CHO_2K required lower generator driven temperature and showed less corrosive, lower density and viscosity than H_2O + LiBr [34].

An effective way to reduce the risk of crystallization in absorption cycles is to add some other salts listed before into LiBr solution. Besides, H_2O + LiBr + LiI + $LiNO_3$ + LiCl was recommend due to less corrosivity and crystallization temperature about 35 °C lower than that of H_2O + LiBr [35]. Solubility, heat capacity and density of H_2O + LiBr + LiI + $LiNO_3$ + LiCl (salt mole ratio = 5:1:1:2) were measured and correlated using empirical polynomial equations [36]. Experiments were finished on a water-cooled vertical smooth tube within the temperature of cooling water of 30–45 °C. The absorption fluxes achieved with this combination at the concentration of 64.2% were around 60% higher than those of H_2O + LiBr at a concentration of 57.9%. Besides, this combination was also simulated in a sea water purification system using absorption transformers [37]. H_2O + LiBr + LiNO3 + LiI + LiCl (LiBr:LiNO3:LiI:LiCl mole ratio = 5:1:1:2) was simulated in a double-effect series-flow absorption chiller and showed no crystallization problem in an air-cooled absorption chiller [38].

A high temperature absorption working pair named "Alkitrate" was proposed [39,40], which was consisted of alkali–metal nitrate salts and H_2O. This working pair could reach a higher output temperature of 260 °C in the absorption transformer without losing the COP when compared with H_2O + LiBr. However, this combination was quite limited at low temperatures [41].

It is known that ionic liquids are the mostly salts with a melting point of below 100 °C, which are composed of organic cations and inorganic anions. Recently, it has been found that the ionic liquids possess considerable potential applications in industrial catalysis, separation processes, electrochemical and other industrial processes because of their unique physical and chemical properties, such as negligible vapor pressure, strong solubility to many organic and inorganic substances, wide liquid phase range, strong stability in the air and H_2O, etc. [42–49].

NaOH, KOH, CsOH and H_2O were used as working fluids in absorption heat pumps [50–52]. Due to significant wider solution field of H_2O and hydroxide than that of H_2O and LiBr, the absorbent was combined by NaOH and KOH (mass ratio = 1:1) using H_2O as refrigerant [50]. This working fluid was experimented in a double effect absorption heat pump, which could reach the COP of 2.1 with a temperature lift of 25 °C. Meanwhile, the same working fluid was analyzed in a double effect absorption heat pump with a heating capacity of about 45 kW [52].

Aqueous ternary hydroxide working fluid consisted with NaOH + KOH + CsOH (mass ratio = 40:36:24) was operated satisfactorily for generator temperatures between 130 °C and 160 °C. On the other side, this combination had lower heat and mass transfer coefficients than H_2O + LiBr due to its high viscosity and corrosion problem at high temperatures. It was found that this alternative mixture might be operated with a higher range of condenser and absorber temperatures, which could allow the use with higher temperature lifts and a smaller risk of crystallization [53,54].

Solubilities and vapour pressures of H_2O + LiBr + $H_2N(CH2)_2OH$ system at three different ratios (mass ratio = 3.5, 4, and 4.5) were measured [55]. H_2O + LiBr + $LiNO_3$ was found to be an alternative to the conventional LiBr + H_2O with higher COP and less corrosivity [56,57], which was simulated and compared with H_2O + LiBr in the absorption heat pump [58].

They performed both the absorption/condensation of H_2O vapor in the falling film apparatus and surface tension measurements of LiBr + H_2O with 2EH and finally concluded that surfactant transported to H_2O vapor by the boil-off plays a dominant role in inducing Marangoni convection [59].

The physical properties of H_2O + LiBr + $HO(CH_2)_3OH$ (mass ratio = 3.5:1) were measured and correlated [60]. A comprehensive model was presented for an air-cooled double effect absorption system using H_2O + LiBr + $HO(CH_2)_3OH$ (mass ratio = 3.5:1), which could increase the COP by 3% and reduce the solution flow rate due to a higher concentration than that with H_2O + LiBr [26,61].

H_2O + LiBr + LiI + $HO(CH_2)_3OH$ was proposed as an alternative to the H_2O + LiBr and showed better heat and mass transfer coefficient than H_2O + LiBr in experiments, and this working fluids could be applied in the air-cooled absorption chillers with wide operation range [62,63].

Initial physical and thermal properties of H_2O + LiBr + $LiNO_3$ + $HO(CH_2)_3OH$ (LiBr/$LiNO_3$ mole ratio = 4:1,

$(LiBr + LiNO_3)/HO(CH_2)_3OH$ mass ratio = 3.5:1) were measured, which could work in the absorption cycles [64].

$LiBr + LiI + HO(CH_2)_3OH + H_2O$ (LiBr:LiI mole ratio = 4:1 and $(LiBr + LiI)/HO(CH_2)_3OH$ mass ratio = 4:1) system was being considered for an absorption chiller by measuring the heat capacities and differential heats of dilution [65].

The working pairs H_2O + EMISE was considered as a potential working pair [66]. The vapor pressure, heat capacity and density of the EMISE + H_2O system were measured and correlated [67], which verified the availability of being used in absorption cycles.

The data obtained for the H_2O + LiCl pair are compared with published data for the H_2O + LiBr pair for identical conditions of temperatures [68].

Thermodynamic analysis of a H_2O-based vapor absorption cycle with four binary mixtures (H_2O + LiBr, H_2O + NaOH, H_2O + LiCl), five ternary mixtures $H_2O + LiBr + LiI$, $H_2O + LiCl + LiNO_3$, $H_2O + LiBr + ZnBr_2$, H_2O + LiBr + LiSCN and seven quaternary mixtures $H_2O + LiBr + LiCl + ZnCl_2$, $H_2O + LiBr + ZnCl_2 + CaBr_2$, $H_2O + LiBr + ZnBr_2 + LiCl$, $H_2O + LiBr + LiI + C_2H_6O_2$, H_2O + NaOH + KOH + CsOH, $H_2O + LiNO_3 + KNO_3 + NaNO_3$, $H_2O + LiCl + CaCl_2 + Zn(NO_3)_2$ were simulated in absorption refrigeration systems. And results revealed that the H_2O + LiCl was better from the point view of cut-off temperature and circulation ration and $H_2O + LiBr + LiCl + ZnCl_2$ was better from the COP and efficiency ratio [69].

2.3. Series of refrigerant using alcohol

The main advantages of working fluids using alcohol are: high thermal stability, high output temperature and satisfying pressure–temperature–concentration diagram. However, most of them have the same toxicity as NH_3.

Absorption heat transformers with TFE + NMP, TFE + E181 and TFE + PYR were compared with each other, and H_2O + LiBr was superior to TFE + NMP, TFE + E181 and TFE + PYR when the output temperature was below 150 °C, which was the maximum output temperature for H_2O + LiBr because of corrosiveness and crystallization problems. TFE + NMP, TFE + E181 and TFE + PYR are all stable at higher temperatures, up to 200 °C [70].

TFE + NMP was firstly proposed due to its advantages such as wide working temperature range, lower working pressure and good safety level [71,72].

With the developments of absorption cycles driven by low temperature heat sources, such as solar energy and low grade waste heat in chemical industries, working fluids like $H_2O + NH_3$ were prior choices which required cold at 0 °C and could be driven by heat resources of 70–100 °C, TFE + TEGDME was considered in many works as an alternative choice in such applications [73–78]. The thermodynamic properties of TFE, E181 and solution TFE + E181 were given [70,74,76]. A modular software package was developed to compare TFE + TEGDME and $H_2O + NH_3$ in vapor exchange double-lift absorption cycles [77]. An increase of 15% of COP was found with TFE + TEGDME when compared with $H_2O + NH_3$.

TFE + E181 was simulated in the double effect absorption heat transformers, which could reach the COP of 0.58 with a gross temperature lift of 30 °C [78].

TFE + PYR was compared with H_2O + LiBr, TFE + NMP, TFE + E181 for the absorption heat transformer, which indicated that H_2O + LiBr was suitable at lower operating temperatures, while TFE + NMP, TFE + E181 and TFE + PYR were suitable at higher operating temperatures [70].

TFE has the activated hydrogen atom available for interaction with a proton acceptor, while quinoline acts as an electron donor that can achieve effective hydrogen bonding with TFE. This

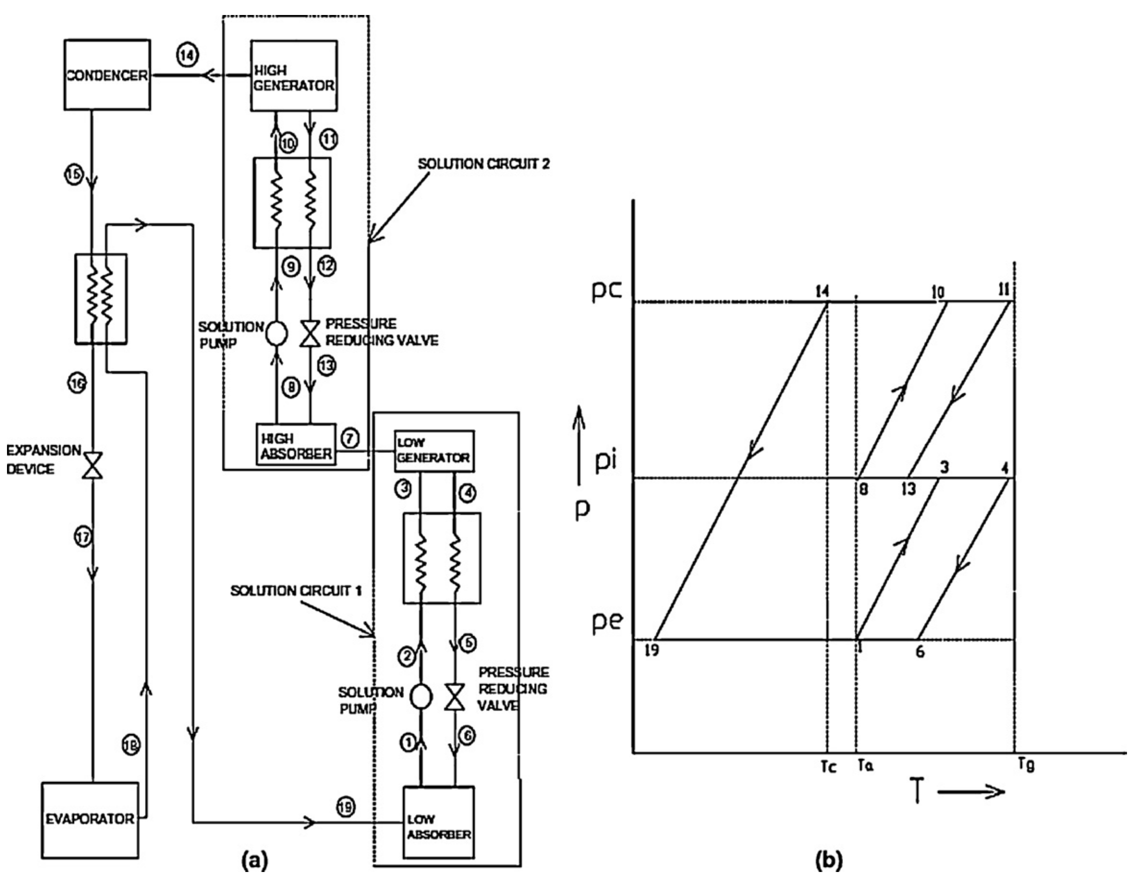


Fig. 2. Half effect vapour absorption cycle (a) and schematic (b) on log *p*–*T* coordinates[90].

working pair was compared with H_2O + LiBr and H_2O + NH_3 in double effect cycles, and simulation results verified its possibility to be an alternative of H_2O + LiBr and H_2O + NH_3 [79,80].

2.4. Series of refrigerant using halogenated hydrocarbon

H_2O + NH_3 and H_2O + LiBr were employed in most absorption cycles currently. However, The H_2O + NH_3 combination requires a heat source temperature above 120 °C for cooling and refrigeration to less than 0 °C. Such a system is a high-pressure system that requires a rectification column. NH_3 has acceptable thermo physical properties, but it is a flammable, toxic, strongly irritant fluid, and is corrosive to copper. The H_2O + LiBr solution can be used with a heat source temperature above 70 °C for air-conditioning but not for cooling and refrigeration because of the limitation for the evaporator temperature over 0 °C. This system operates under vacuum and does not require a rectification column. The H_2O + LiBr solution is corrosive and more viscous than water. Thus corrosion inhibitors are required. With a view to overcoming these limitations, the working fluids based on environmentally acceptable fluorocarbon (HFC) refrigerants and organic absorbents have been presented.

R21, R22, R30, R31, R133a, R124a, R134a were compared in the absorption refrigeration cycle, and R21 shown highest COP due to its larger latent heat of vaporization [81]. However, high crosstivity on copper limited its application.

R134a was employed as refrigerant with R134a + DMETEG, MCL, DMEU as absorbent, respectively. It was found that COPs of these combinations were similar and R134a + DEMTEG owned the lowest cycle ratio [82]. R134a + DMEU, R134a + MCL and R134a + DMETEG were all simulated in the absorption heat pumps and obtained similar COP, but the value off for R134a + DMTEG was lower than for

Table 1
Characterizes comparison of different working fluids.

Working pair	Ref. no.	Absorption cycle	Remarks
NH_3 + H_2O + LiBr	[11–14]	AC	Significantly lower H_2O content of vapor entering the rectifier; higher COP than NH_3 + H_2O
NH_3 + $LiNO_3$	[15]	AC	Lower generation temperature than NH_3 + H_2O
NH_3 + H_2O + NaOH	[16]	AC	Improve the separation of NH_3 and reduce driving temperature with higher COP
H_2O + LiBr + $(CH_2OH)_2$	[25]	AHT	Similar thermal properties as LiBr + H_2O with a higher solubility of about 80%
LiBr + $H_2N(CH_2)_2OH$ + H_2O	[26]	AC	Less crystallization risk than LiBr + H_2O in air cooled absorption chiller; high viscosity; corrosion
LiBr + $HO(CH_2)_3OH$ + H_2O	[26]	AC	Less crystallization risk than LiBr + H_2O in air cooled absorption chiller; high viscosity; corrosion
LiBr + $(HOCH_2CH_2)_2NH$ + H_2O	[26]	AC	Less crystallization risk than LiBr + H_2O in air cooled absorption chiller; high viscosity; corrosion; less heat and mass transfer coefficient
H_2O + KNO_3	[27,28]	AHT	Low corrosive and better heat and mass transfer than H_2O + NH_3
H_2O + $CaCl_2$	[29]	AHT	High COP than H_2O + LiCl; readily available and environmental friendly; less corrosive than LiBr + H_2O
H_2O + LiBr + CH_3COOK H_2O + LiBr + $CH_3CH(OH)COONa$	[30]	AHP	Readily available and environmentally friendly, suitable for moderate temperature applications than LiBr + H_2O
H_2O + CHO_2Na + LiBr H_2O + CHO_2K + LiBr	[30–34]	AC	Good thermodynamic properties, low toxicity and non-flammability
H_2O + LiBr + LiI + $LiNO_3$ + LiCl	[35–38]	AC	Higher COP, lower generation temperature, less crossivity than LiBr + H_2O
Alkitrate	[39–41]	AHT	Output temperature of 260 °C without losing the COP compared with H_2O + LiBr; limited in low temperatures
NaOH + KOH + H_2O	[50,52]	AHP	Significant wider solution field, higher temperature lift, better COP than LiBr + H_2O
NaOH + KOH + CsOH + H_2O	[53,54]	AHT	Higher temperature lifts and a smaller risk of crystallization; high viscosity and corrosion
H_2O + LiBr + $LiNO_3$	[56–58]	AHP	An alternative to the conventional LiBr + H_2O with higher COP and less corrosivity
H_2O + LiBr + $HO(CH_2)_3OH$	[60,61]	AHP; AC	Higher COP with lower flow rate than LiBr + H_2O; air-cooled; anti-crystallization enhanced by $HO(CH_2)_3OH$
H_2O + LiBr + LiI + $HO(CH_2)_3OH$	[62,63]	AC	Better heat and mass transfer coefficient than LiBr + H_2O; air-cooled
H_2O + LiBr, H_2O + NaOH, H_2O + LiCl, H_2O + LiBr + LiI, H_2O + LiCl + $LiNO_3$, H_2O + LiBr + $ZnBr_2$, H_2O + LiBr + LiSCN, H_2O + LiBr + LiCl + $ZnCl_2$, H_2O + LiBr + $ZnCl_2$ + $CaBr_2$, H_2O + LiBr + $ZnBr_2$ + LiCl, H_2O + LiBr + LiI + $C_2H_6O_2$, H_2O + NaOH + KOH + CsOH, H_2O + $LiNO_3$ + KNO_3 + $NaNO_3$, H_2O + LiCl + $CaCl_2$ + $Zn(NO_3)_2$	[69]	AC	Sixteen working pairs were compared in AC, which was aimed to improve COP and flow rate
TFE + NMP	[70–72]	AHT	Working temperature range, lower working pressure and good safety level
TFE + E181	[70,74,76,78]		Temperature lift over 30 °C without losing COP
TFE + TEGDME	[73–78]	AHP	Lower driving temperature, higher COP than NH_3 + H_2O
R134a + DMETEG, R134a + MCL, R134a + DMEU	[82]		No rectification; no toxic and corrosivity
R125 + NMP, R125 + DMAC, R125 + MCL, R125 + DMPU and R125 + DMETEG	[87]	TPL	Low-potential heat-sources (70–120) for cooling and refrigeration; not toxic or corrosive; environmentally acceptable; no rectification
R124 + DMAC, R124 + NMP, R124 + MCL, R124 + DMEU, R124 + DMETEG	[88]	AC	Lower COP values than R22 series, higher COP than R134a series. The working fluids based on R124 had lower *f* values; driven by low potential heat sources for subzero temperatures
R134a + DMAC	[90,91]	AC	Effectively increased COP than NH_3 + H_2O with a half effect cycle
Acetone + $ZnBr_2$	[94]	AHP	Generating temperature of 50 °C
H_2O + monomethylamine	[96–98]	AHP	Similar properties as NH_3 with lower vapor pressure

the other two pairs, therefore, it was the best of the three candidate working pairs [93].

Single stage and double stages absorption heat pumps employing R22, R134a and R32 as refrigerant and DMAC, DMEU, DMETEG, NMP and MCL as absorbent are compared, respectively, and the performance of R22 was better than R124 and R134a could not work in the single stage absorption heat pump [82].

Pressure–temperature–concentration diagram and the enthalpy–concentration diagram of R22 and DMEDEG were given, which showed the possibility of being used in absorption cycles [83,92].

Thermal equations of five kinds of working fluids combined with R134a, R143a, R32 and R125 were investigated by giving thermodynamic properties charts [84–86].

Concerning the working fluids based on the refrigerant R125 and the six absorbents, it was found that the solution R125 + DMEU showed the best performances followed by R125 + NMP, R125 + DMAC, R125 + MCL, R125 + DMPU and R125 + DMETEG. The calculated COP's in the TPL cycle (triple-pressure level single-stage absorption cycle) were in the range of 0.45–0.59 and the circulation ratios were in the range of 2–5 [87].

Possibility of using R124 as refrigerant and DMAC, NMP, MCL, DMEU and DMETEG was studied, respectively, meanwhile, an improved method of calculation the liquid and gas phases and the excess thermal properties of the working fluids as a function of the system temperature and pressure based on their experimental data. R124 + DMAC was recommended to be using as an alternative working fluid in the absorption chillers [88].

The combined vapor absorption and compression system and absorption system all using DMF + R22 as the working fluid were simulated and compared, and results indicated the superiority of the combined system over the absorption system [89].

In order to decrease of the driven temperature of absorption refrigeration cycles, a half effect cycle shown in Fig. 2 is feasible with heat input temperatures below that of a single stage cycle. When compared with H_2O + NH3, R134a + DMAC could give a significant improvement in COP in this cycle, and an average increase in COP of 33% could be obtained within the evaporator temperature range of −5 to 5 °C [90,91].

2.5. Series of refrigerant using other mediums

There are also many efforts on developing new working fluids basing on other absorbents.

In order to use low generator temperatures (47–60 °C) generated by solar collectors, acetone + $ZnBr_2$ was taken into account to be an alternative working fluid through theoretical and experimental ways. Results showed that it could be operated at a generating temperature of 50 °C without problems [94].

Two ternary systems of the ethylamine + H_2O + LiBr (H_2O:LiBr mass ratio = 2:1) and the ethylamine + H_2O + $LiNO_3$ (H_2O:$LiNO_3$ mass ratio = 2:1) were proposed in order to improve the performance characteristics, to reduce the dangerousness, the toxicity, and the cost of absorption cycles [95].

H_2O + monomethylamine was employed in the absorption heat pump when H_2O was used as the absorbent and reasonable temperature ranges of generation, condensation, evaporation and absorption were listed for cooling and heating cases, respectively [96–98].

3. Discussions

In order to choosing working fluids conveniently, a comparison of working fluids was presented in Table 1.

Water was chosen as the refrigerant in most new working fluids studied as far due to its high evaporation latent, environmental friendly and low cost. A basic rule to choose working fluids for absorption cycles is the absorption performance forecast according to operation conditions with acceptable limitations, such as crystallization problem, environmental limit and material requirement. Basing on current researches, LiBr + H_2O and NH_3 + H_2O with different additives will play a much more important role, however, working fluids like HFCs will be more promising, when absorption cycles are employed in special cases, such as solar energy, ground heat and low grade heat in industrials.

4. Conclusions

This paper describes a number of researches of working fluids of absorption cycles, which contain absorption heat pumps, absorption chillers and absorption transformers. Absorption cycles will play a more important role in the future due to its advantages in energy saving field. The research aspect of improving working fluids is quite essential in its progress. Most of absorption cycles are using H_2O as the refrigerant, when different additives are added into the solution. New working fluids have been developed in special absorption cycles, for example, driven by solar, underground heat and waste heat in industries.

It is hoped that this paper will draw wider interest in the working fluids of absorption cycles. It should be useful for choosing working fluids of absorption cycles in different applications in practice.

Acknowledgements

The authors gratefully acknowledge financial support from the National Science and Technology Support Plan of Peoples Republic of China (No.: 2007BAB23B01) and the key projects of the Beijing Municipal Science and Technology Plan (No.: D07040600560701).

References

[1] Gosney WB. Principle of refrigeration. Cambridge University Press; 1982.
[2] Perez BH. Absorption heat pump performance for different types of solution. International Journal of Refrigeration 1984;7:115–22.
[3] Holmberg P, Berntsson T. Alternative working fluids in heat transformers. ASHRAE Transactions 1990;96:1582–9.
[4] Pongsid S, Satha A, Supachart C. A review of absorption refrigeration technologies. Renewable and Sustainable Energy Reviews 2001;5:343–72.
[5] Da WS. Comparison of the performances of NH_3–H_2O, NH_3–$LiNO_3$ and NH_3–NaSCN absorption refrigeration systems. Energy Conversion and Management 1998;39:357–68.
[6] El-Sayed YM, Tribus M. Thermodynamic properties of H_2O–NH_3 mixtures: theoretical implementation for use in power cycle analysis. ASME Pub AES 1985;1:89–95.
[7] Ziegler B, Trepp C. Equation of state for NH_3–H_2O mixtures. International Journal of Refrigeration 1984;7:101–6.
[8] Herold KE, Han K, Moran MJ. AMMWAT: a computer program for calculating the thermodynamic properties of NH_3 and H_2O mixtures using a Gibbs free energy formulation. ASME Pub AES 1988;4:65–75.
[9] Patek J, Klomfae J. Simple function for fast calculations of selected thermodynamic properties of NH_3–H_2O system. International Journal of Refrigeration 1995;18:228–34.
[10] Best R, Eisa MA, Holland FA. Thermodynamic design data for absorption heat pump systems operating on NH_3–H_2O. Part 2. Heating. Heat Recovery System & CHP 1987;7:177–85.
[11] Mclinden MO, Radermacher R. An experimental comparison of NH_3–H_2O and NH_3–H_2O–LiBr mixtures in an absorption heat pump. ASHRAE Transactions 1985;191:1837–46.
[12] Peters R, Greb O, Korinth C. Vapor–liquid equilibria in the system NH_3 + H_2O + LiBr:1 measurement at T = 303–423 K and p = 0.1–0.5 Mpa. Journal of Chemical and Engineering Data 1995;40:769–74.
[13] Peters R, Korinth C, Jurgen UK. Vapor–liquid equilibria in the system NH_3 + H_2O + LiBr:2 data correlation. Journal of Chemical and Engineering Data 1995;40:775–83.
[14] Radermacher R, Alefeld G. Wassrige LiBr losung als absorber fur NH_3K und methlyamin. Breennstoff, waerme, kraft 1982;34:31–8.

[15] Kaushik SC, Kumar R. Thermodynamic study of a two-stage vapor absorption refrigeration system using NH_3 refrigerant with liquid–solid absorbent. Energy Conversion & Management 1985;25:427–31.
[16] Steiu S, Salavera D, Bruno JC, Coronas A. A basis for the development of new NH_3–H_2O–sodium hydroxide absorption chillers. International Journal of Refrigeration 2009;32:577–87.
[17] Berestneff AA. Absorption refrigeration. Mechanical Engineering 1949;72:216–35.
[18] McNeely LA. Thermodynamic properties of aqueous solutions of LiBr. ASHRAE Transactions 1979;85:413–34.
[19] Patterson MR, Perez-Blanco H. Numerical fits of properties of lithium-bromide H_2O solutions. ASHRAE Transactions 1988;94:2059–77.
[20] Lee RJ, DiGuilio RM, Jeteter SM, Teja AS. Properties of LiBr–H_2O solutions at high temperatures and concentrations. Part II. Density and viscosity ASHRAE. Transactions 1990;96:709–14.
[21] Jeter SM, Moran JP, Teja AS. Properties of LiBr–H_2O solutions at high temperatures and concentrations. Part III. Specific heat. ASHRAE Transactions 1992;98:137–49.
[22] Lenard JLY, Jeter SM, Teja AS. Properties of LiBr–H_2O solutions at high temperatures and concentrations. Part IV. Vapor pressure. ASHRAE Transactions 1992;98:167–72.
[23] Eisa MAR, Rashed GA, Devotta S. Thermodynamic design data for absorption heat pump systems operating on H_2O–LiBr. Part 1. Heating. Journal of Applied Energy 1986;5:71–82.
[24] Patil HR, Chaudhari SK, Katti SS. Thermodynamic design data for absorption heat pump systems operating on H_2O–lithium iodide. Part 2. Heating. Heat Recovery & CHP 1991;11:351–60.
[25] Best R. Modelling of single-effect stage and advanced absorption heat transformers operating with H_2O/carrol mixture. Applied Thermal Engineering 1997;17:1111–2.
[26] Kim JS, Park Y, Lee H. Performance evaluation of absorption chiller using LiBr + $H_2N(CH_2)_2OH$ + H_2O, LiBr + $HO(CH_2)_2OH$ + H_2O, and LiBr + $(HOCH_2CH_2)_2NH$ + H_2O as working fluids. Applied Thermal Engineering 1999;19:217–25.
[27] Kim JS, Park Y, Lee H. Densities of the water + lithium bromide + ethanolamine system. Journal of Chemical Engineering Data 1996;41:678–80.
[28] Iyoki S, Uemura T. Studies on the water–lithium bromide–ethylene glycol absorption refrigeration machine. Reito 1981;56:279–88.
[29] Rosa MBR, Victor MAG, Alfonso GG. Performance modeling of single and double absorption heat transformers. Current Applied Physics 2010;10: 244–8.
[30] Antonio DL, Marina D, Juan FR. Vapour pressure, densities, and viscosities of the (H_2O + LiBr + potassium acetate) system and (H_2O + LiBr + sodium lactate) system. Journal of Chemical Thermodynamics 2006;38:123–9.
[31] Antonio DL, Marina D, Juan FR. Absorption of H_2O vapor into new working fluids for absorption refrigeration systems. Industrial & Engineering Chemistry Research 2007;46:345–50.
[32] Antonio DL, Marina D, Juan FR. Vapor pressures, densities, and viscosities of the (H_2O + LiBr + sodium formate) system and (H_2O + LiBr + potassium formate) system. Journal of Chemical Engineering Data 2003;48:18–22.
[33] Antero A. Potassium formate as a secondary refrigerant. International Journal of Refrigeration 1997;20:276–82.
[34] Antonio DL, Marina D, Carolina M, Jose V, Juan FR. Performance evaluation and simulation of a new absorbent for an absorption refrigeration system. International Journal of Refrigeration 2004;27:324–30.
[35] Mahmoud B, Manel V, Marc M, Alberto C. Absorption of H_2O vapour in the falling film of H_2O-(LiBr + LiI + $LiNO_3$ + LiCl) in a vertical tube at air-cooling thermal conditions. International Journal of Thermal Science 2005;44: 491–8.
[36] Salavera D, Esteve X, Patil KR, Mainar AM. Coronas solubility, heat capacity, and density of LiBr + Lithium Iodide + Lithium Nitrate + Lithium chloride aqueous solutions at several compositions and temperatures. Journal of Chemical Engineering Data 2004;49:613–9.
[37] Bourouis M, Coronas A, Romero RJ, Siqueiros J. Purification of sea H_2O using absorption heat transformers with H_2O-(LiBr + LiI + $LiNO_3$ + LiCl) and low temperature heat sources. Desalination 2004;166:209–14.
[38] Lee HR, Koo KK, Jeong S, Kim JS, Lee H, Oh YS. Thermodynamic design data and performance evaluation of the H_2O + LiBr + lithium iodide + lithium nitrate + lithium chloride system for absorption chiller. Applied Thermal Engineering 2000;20:707–20.
[39] Davidson WF, Erickson DC. 260 °C aqueous absorption working pair under development. IEA Heat Pump Centre Newsletter 1986;4:29–31.
[40] Howe LA, Erickson DC. 260 °C absorption working pair ready for field test. IEA Heat Pump Centre Newsletter 1990;8:7–9.
[41] Zhuo CZ, Machielsen CHM. Performance of high-temperature absorption heat transformers using alkitrate as the working pair. Applied Thermal Engineering 1996;16:255–62.
[42] Kim K, Shin B, Lee H, Ziegler F. Refractive index and heat capacity of 1-butyl-3-methylimidazolium bromide and 1-butyl-3-methylimidazolium tetrafluoroborate, and vapor pressure of binary systems for 1-butyl-3-methylimidazolium bromide + trifluoroethanol and 1-butyl-3-methylimidazolium tetrafluoroborate + trifluoroethanol. Fluid Phase Equilibria 2004;218:215–20.
[43] Stoecker WF, Jones JW. Refrigeration and air conditioning. New Delhi: Tata McGraw-Hill; 1982.
[44] Ziegler F. Recent developments and future prospects of sorption heat pump systems. International Journal of Thermal Sciences 1999;38:191–208.
[45] Huddleston JG, Willauer HD, Swatloski RP, Visser AE, Rogers RD. Room temperature ionic liquids as novel media for clean liquid extraction. Chemical Communication 1998;16:1765–6.
[46] Nebig S, Bolt R. Measurement of vapor-liquid equilibria (VLE) and excess enthalpies (HE) of binary systems with 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide and prediction of these properties and gamma infinite using modified UNIFAC (Dortmund). Fluid Phase Equilibrium 2007;258:168–78.
[47] Li QS, Xing FY, Isobaric J. Vapor-liquid equilibrium for isopropanol + water + 1-ethyl-3-methylimidazolium tetrafluoroborate. Chemical Engineering Data 2008;53:275–9.
[48] Seddon KR, Stark A, Torres MJ. Influence of chloride, water, and organic solvents on the physical properties of ionic liquids. Pure Applied Chemical 2000;72:2275–87.
[49] Rockenfeller U, Langeliers J. Aqueous absorption fluids. Chicago: Gas Research Institute Annual Report; 1988.
[50] Flamensbeck M. A cost effective absorption chiller with plate heat exchanger using H_2O and hydroxides. Applied Thermal Engineering 1998;118: 413–25.
[51] Best R, Holland FA. A study of the operating characteristics of an experimental absorption cooler using ternary systems. International Journal of Energy Reservation 1990;14:553–61.
[52] Flamensbeck M, Summerer F, Riesch P, Ziegler F, Alefeld G. A cost effective absorption chiller with plate heat exchangers using H_2O and hydroxides. Applied Thermal Engineering 1998;18:413–25.
[53] Stephan K, Schmitt M, Hebecker D, Bergman T. Dynamics of a heat transformer working with the mixture NaOH–H_2O. International Journal of Refrigeration 1997;20:483–95.
[54] Romero RJ, Rivera W, Pilatowsky I, Best R. Comparison of the modeling of a solar absorption system for simultaneous cooling and heating operating with an aqueous ternary hydroxide and with H_2O/LiBr. Solar Energy Materials & Solar cells 2001;70:301–8.
[55] Kim JS, Park Y, Lee H. Solubilities and vapour pressure of the H_2O + LiBr + ethanolamine system. Journal of Chemical Engineering Data 1996;41:279–81.
[56] Iyoki S, Yamanaka R, Uemura T. Physical and thermal properties of the H_2O–LiBr–lithium nitrate system. International Journal of Refrigeration 1993;16:191–200.
[57] Uemura T, Hasaba S. Studies on the LiBr–H_2O absorption refrigeration machine. Technology Reports of Kansai University; 1964.
[58] Sun J, Fu L, Zhang SG. Performance calculation of single effect absorption heat pump using LiBr + $LiNO_3$ + H_2O as working fluid. Applied Thermal Engineering 2010;30:2680–4.
[59] Kulankara S, Herold KE. Theory of heat/mass transfer additives in absorption chillers. International Journal of HVAC&R Research 2000;6: 369–79.
[60] Park Y, Kim JS, Lee H. Physical properties of the LiBr + 1,3-propanediol + H_2O system. International Journal of Refrigeration 1997;20:319–25.
[61] Yoon JI, Kwon OK. Cycle analysis of air-cooled absorption chiller using a new working solution. Energy 1999;24:795–809.
[62] Park SB, Lee H. Heat and mass transfer of the new LiBr-based working fluids for absorption heat pump. Industrial & Engineering Chemistry Research 2002;41:1378–85.
[63] Kim JS, Lee H. Solubilities. Vapor pressures, densities, and viscosities of the LiBr + LiI + $HO(CH_2)_3OH$ + H_2O system. Journal of Chemical Engineering Data 2001;46:79–83.
[64] Park Y, Kim JS, Lee H. Density. Vapor pressure, solubility, and viscosity for H_2O + LiBr + lithium nitrate + 1,3-propanediol. Journal of Chemical Engineering Data 1997;42:145–8.
[65] Kim JS, Lee HS, Lee H. Thermal property measurements and enthalpy calculation of the LiBr + lithium iodide + 1,3-propanediol + H_2O system. International Journal of Thermophysics 2000;21:1407–18.
[66] Zuo GL, Zhao ZC, Yan SH, Zhang XD. Thermodynamic properties of a new working pair: 1-ethyl-3-methylimidazolium ethylsulfate and H_2O. Chemical Engineering Journal 2010;156:613–7.
[67] He ZB, Zhao ZC, Zhang XD, Feng H. Thermodynamic properties of new heat pump working pairs: 1,3-dimethylimidazolium dimethylphosphate and H_2O, ethanol and methanol. Fluid Phase Equilibrium 2010;298:83–91.
[68] Grover GS, Devotta S, Holland FA. Thermodynamic design data for absorption heat pump systems operating on H_2O–lithium chloride. Part 2. Heating. Heat Recovery Systems & CHP 1988;8:419–23.
[69] Saravanan R, Maiya MP. Thermodynamic comparison of H_2O-based working fluid combination for a vapour absorption refrigeration system. Applied Thermal Engineering 1998;18:553–68.
[70] Yin J, Shi L, Zhu MS, Han LZ. Performance analysis of an absorption heat transformer with different working fluid combinations. Applied Energy 2000;67:281–92.
[71] Xu S, Liu Y, Zhang L. Performance research of self regenerated absorption heat transformer cycle using TFE-NMP as working fluids. International Journal of Refrigeration 2001;24:510–8.
[72] Mashimo K. Nowadays working fluids used in absorption chillers-TFE/NMP. Refrigeration (Japan) 1993;789:72–5.
[73] Stephan K. Heat transformation with the ternary working fluid TFE-H_2O-E181. International Journal of Refrigeration 1994;16:120–8.
[74] Coronas A. Absorption heat pump with the TFE-TEGDME and the TFE-H_2O-TEGDNE system. Applied Thermal Engineering 1996;16:335–45.

[75] Kawada A, Otake M, Toyofuku. Absorption compression heat pumps using TFE-E181: environment-friendly technologies for the 21st century. Tokyo 1991;12:1–6.
[76] Stephan K, Henger R. Heat transformation with the ternary working fluid TFE-H_2O-E181. International Journal of Refrigeration 1993;16:120–8.
[77] Medrano M, Bourouis M, Coronas A. Double-lift absorption refrigeration cycles driven by low-temperature heat source using organic fluid mixtures as working pairs. Applied Energy 2001;68:173–85.
[78] Zhao ZC, Zhang XD, Ma XH. Thermodynamic performance of a double-effect absorption heat-transformer using TFE/E181 as the working fluid. Applied Energy 2005;82:107–16.
[79] Kim KS, Lee JW, Kim JS, Lee H. Heat capacity measurement and cycle simulation of the trifluoroethanol (TFE) + quinoline mixture as a new organic working fluid used in absorption heat pump. Korean Journal of Chemical Engineering 2003;20:762–7.
[80] Kim KS, Lee H. Densities, viscosities and surface tensions of the trifluoroethanol + quinoline system. Journal of Chemical Engineering Data 2002;47:216–8.
[81] Eiseman BJ. Why refrigerant 22 should be favored for absorption refrigeration. ASHRAE Journal 1959;12:45–50.
[82] Jelinek M, Borde I. Single and double stage absorption cycles based on fluorocarbon refrigerants and organic absorbents. Applied Thermal Engineering 1998;18:765–71.
[83] Ando E, Takeshita I. Residential gas-fired absorption heat pump based on R22-DEGDME pair. Part 1. Thermodynamics properties on R22-DEGDME pair. International Journal of Refrigeration 1984;7:181–5.
[84] Tilner RR. Thermodynamic properties of pure and blended hydrofluorocarvon (HFC) refrigerants. Japan society of refrigerating and air conditioning engineers; 1998.
[85] Nagel M, Bier K. Vapour-liquid equilibrium of ternary mixtures of the refrigerants R32, R125 and R134a. International Journal of Refrigeration 1995;18:534–43.
[86] Nagel M, Bier K. Vapour-liquid equilibrium of ternary mixture of the refrigerants R125, R134a and R143a. International Journal of Refrigeration 1996;19:264–71.
[87] Jelinek M, Borde I. Working fluids for absorption heat pumps based on R125 (pentafluoroethane) and organic absorbents. In: International Sorption Heat Pumps Conference. 1999. p. 205–8.
[88] Borde I, Jelinek M, Daltrophe NC. Working fluids for an absorption system based on R124 and organic absorbents. International Journal of Refrigeration 1997;20:256–66.
[89] Agarwal RS. Performance analysis of R22-DMF turbo absorption refrigeration systems. Energy Conversion and Management 1987;27:211–7.
[90] Arivazhagan S, Murugesan SN, Saravanan R, Renganarayanan S. Simulation studies on R134a-DMAC based half effect absorption cold storage systems. Energy Conversion and Management 2005;46:1703–13.
[91] Keith H. Absorption chillers and heat pump. CRC Press; 1996.
[92] Dan PD, Murthy SS. Thermodynamic analysis data on vapour absorption heat pump working on R22-DMETEG pair. Heat Recovery Systems and CHP 1988;8:87–93.
[93] Borde I, Jelinek M, Daltrophe NC. Absorption systems based on the refrigerant R134a. International Journal of Refrigeration 1995;18:387–94.
[94] Ali K, Salman A. Thermodynamic analysis of an absorption refrigeration machine with new working fluid for solar applications. Heat Mass Transfer 2008;45:71–81.
[95] Iyoki S, Gouda H, Ootsuda S, Uemura T. Vapour pressure of the ethylamine + H_2O + LiBr system. Journal of Chemical Engineering Data 1998;43:662–4.
[96] Pilatowsky I, Rivera W, Best R. Thermodynamic design data for absorption heat pump systems operating on monomethylamine–H_2O. 1. Cooling. Heat Recovery System & CHP 1995;15:563–70.
[97] Pilatowsky I, Rivera W, Best R. Thermodynamic design data for absorption heat pump systems operating on monomethylamine–H_2O. 2. Heating. Heat Recovery System & CHP 1995;15:571–81.
[98] Pilatowsky I, Rivera W, Best R, Holland FA. Thermodynamic design data for absorption heat pump systems operating on monomethylamine–H_2O. 3. Simultaneous cooling and heating. Heat Recovery System & CHP 1995;15: 583–9.